RADIONUCLIDE X-RAY FLUORESCENCE ANALYSIS. III.

EXAMPLES OF APPLICATION IN PRACTICE
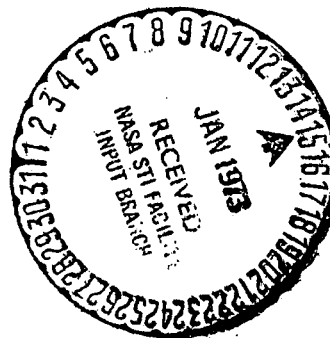
Štefan Varga

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C.   20546   JANUARY 1973

RADIONUCLIDE X-RAY FLUORESCENCE ANALYSIS. III.*
EXAMPLES OF APPLICATION IN PRACTICE

Štefan Varga

ABSTRACT. The aim of this paper is to demonstrate on a number of examples the utilisability and the importance of radionuclide fluorescence analysis as a method of instrumental analysis.

Introduction

Radionuclide fluorescence analysis belongs today among the important physical- chemical analytic methods. Its main advantage is the conceptual, constructional and functional simplicity of the radionuclide sources exciting the radiation [1] and of the fluorescence X-ray radiation detectors. [2]

Analytic methods, based on the excitation of fluorescence radiation by radionuclides, can determine a large number of elements from the entire periodic system. Technically, the process is dependent on the energy of excited fluorescence radiation; therefore it is useful to classify the examples of the element determination by the radionuclide X-ray fluorescence analysis into several groups according to the atomic number of the determined element. Table I documents this.

TABLE 1. ATOMIC NUMBER OF THE DETERMINED ELEMENT AND FLUORESCENCE RADIATION ENERGY

Determined elements z	Fluorescence radiation energy keV
$Z < 20$	<4
$21 < Z < 30$	$4-9$
$31 < Z < 57$	$9-33$
$58 < Z < 71$	$33-55$
$72 < Z$	$55-99$

* II. Part: Chem. listy, Vol. 65, 1971, p. 28.

** Numbers in the margin indicate pagination in the original foreign text.

The sensitivity of the fluorescence analysis decreases with a decrease in atomic number, i.e. with decreasing energy of the K-lines. The observation limit, which is 0.05% for elements with $Z \geq 45$, increases to 1% for Br with $Z=35$.

Determination of light elements
(Z<20)

Characteristic K-series lines of the light elements group (Z<20), i.e. the group from carbon to calcium, have a very low energy: 0.28 - 3.8 keV. Detection of the radiation with such low energy is a serious technical problem.

The only suitable detectors are the proportional counters, because they have a sufficiently high detection efficiency, good resolving power, and a low noise even in the low energy region.

The use of proportional counters filled with argon creates, however, some difficulties connected with resolving the characteristic argon lines (K_α: 2.96 keV) from the lines of the determined element, such as chlorine (K_α: 2.62 keV) and potassium. Similar difficulties appear when other pairs or groups of neighbouring or close elements are determined.

^{55}Fe with an energy of 5.9 keV is mostly used as an excitation radiation source in this energy region. The bremsstrahlung source is usually ^{3}H/Ti with the characteristic energy line of 4.5 keV. ^{3}H/Zr should be also considered, since it emits besides the K-line also the zirconium L-line (Zr - L_α : 2.042 keV), which has an energy corresponding to the excitation conditions of magnesium, aluminum and silicon[3], and even fluorine[4].

Bremsstrahlung sources containing tritium and ^{55}Fe were used also for the determination of magnesium, aluminum, silicon, calcium and iron in cement and in iron ore [5,6,7]. In these processes, the energy resolution of the magnesium, aluminum, and silicon K-lines was not resolved sufficiently. Chemical analysis of the cement and raw materials needed for its production represents a field, in which the radionuclide fluorescence methods are widely applied. The excitation radiation source used for the determination of calcium in cement was, besides iron, also ^{109}Cd[8]. The continuous "on stream" method for determination of calcium by ^{55}Fe[9] is more suitable under operational conditions.

2

The model Fe-Al samples proved that for the composition 50% Fe-50% Al
the sensitivity of 1% Al or Fe, respectively, was achieved by using the brems-
strahlung radiation source and that the aluminum content can be determined even
in the presence of iron from the calibration curve [7]. This was verified by
the determination of the ash content in bituminous coal [7]. The ash-forming
elements Si, Al are the neighbouring elements, and therefore they cannot be
distinguished individually by fluorescence radiation. Iron is usually present
in coal also. The silicon content can be taken as a criterion of ash content.
The ash content in coal can be thus determined from the calibration curve repre-
senting the dependence of Si $-K_\alpha$ line intensity on the percent of the ash-forming
ratio. Figure 1 shows such a curve [7]. The measurement accuracy is ±1.5% of
ash, when the sources $^3H/Ti$ or $^3H/Zr$ (2.6 Ci) respectively, are used, and the
measuring time is ten seconds. The sulphur content of coal [10] was also studied
by a portable analyser with a bremsstrahlung source ($^3H/Ti$). The main mineral
components of coal are usually Al, Si, Ca, Fe, and S. The sulphur content is
between 0-5%; it is determined by a balanced filter pair. The method is based on
the calibration curve shown in Figure 2. The calibration curve was determined
from coal with an ash content 7% and 13%; the sulphur determination is not
affected by the ash content value. The standard deviation is 0.17m of sulphur for
100 seconds measuring time.

A combined method was developed for the CaO and Fe_2O_3 determination in the
raw cement mixture [10]. The radiation sources ^{55}Fe, $^3H/Ti$ or $^3H/Zr$ could be
used for the Ca K-line (3.7 keV) excitation. The $^3H/Zr$ source is most suitable
for the iron K-line (6.4 keV). Therefore ^{55}Fe is used for calcium K-line
excitation; the iron radiation is not excited then. Iron K-lines are excited
by bremsstrahlung of $^3H/Zr$. Although the calcium K-lines are excited as well, they
can be absorbed by an iron filter 0.013 mm thick. Figure 3 shows the dependence
of the Ca-K line intensity on the CaO content in cement. The calibration curve
was obtained from the mixtures with Fe_2O_3 (1.45 - 4.5%) using ^{55}Fe without a
filter. The standard deviation is smaller than 0.1% of CaO when the CaO content
is 45%. Figure 4 gives the calibration curve for the Fe_2O_3 content in cement.
It was obtained by the $^3H/Zr$ excitation radiation and Fe filter (0.013 mm). The
standard deviation is smaller than 0.045% of Fe_2O_3 for a 3% Fe_2O_3 content. The
calibration curve was determined from a mixture with varying CaO content (38.0 -
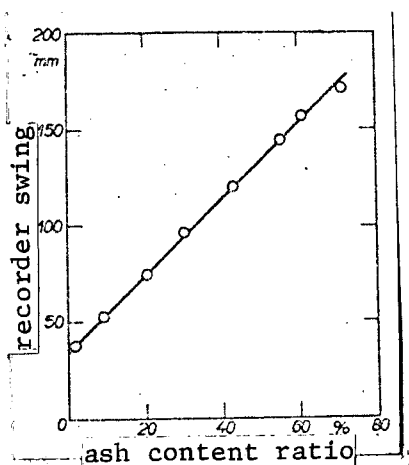50.0%).

3

Figure 1. Calibration curve for the determination of ash content in coal using the silicon K_α line intensity. [7]
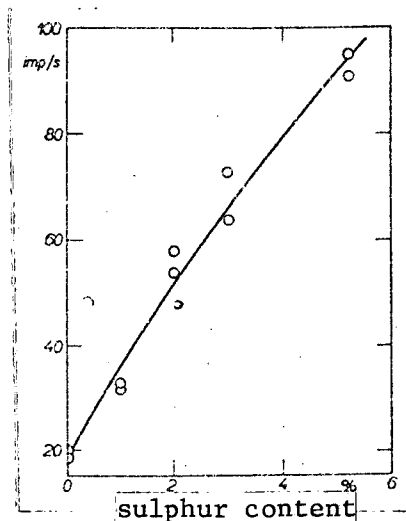

Figure 2. Calibration curve for the determination of sulphur content in coal [10].
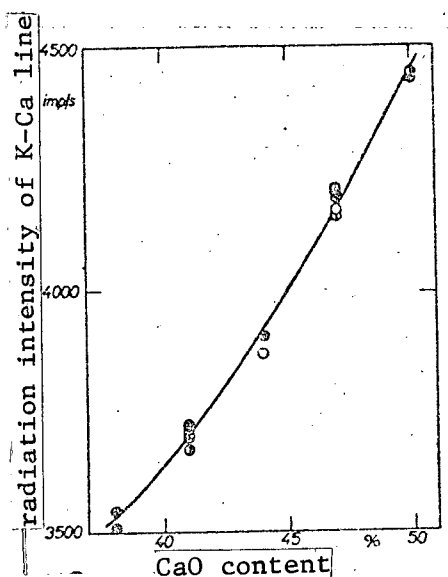

Figure 3. Calibration curve for the determination of CaO content in cement using the calcium K_α line intensity [10].
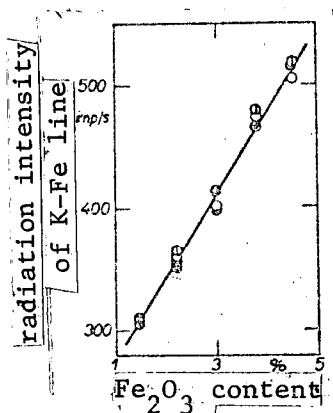
Figure 4. Calibration curve for the determination of Fe_2O_3 content in cement using the iron K_α line intensity [10].

Utilization of the α radiation sources has certain advantages for the fluorescence radiation excitation too.

Efficiency of the fluorescence excitation is about equal for the α radiation /116 and γ radiation, when the elements with atomic numbers of 15 - 20 are used. For lighter elements, the α radiation efficiency is even higher. It increases with a decreasing atomic number up to a maximum at carbon, then decreases rapidly. The backscattered α radiation and α-bremsstrahlung have a negligible intensity [11, 12]. The most important α radiation source for the fluorescence analysis is ^{210}Po(6 m Ci).

4

It is used in connection with the mica window (1 mg/cm^{-2}) or windowless proportional counter [13]. Automatic analysers for cement samples were developed; they use simultaneously ^{210}Po for aluminum, silicon and calcium determination, and ^{3}H/Zr for iron determination [14 - 18].

Determination of elements Sc — Zn
(21<Z<30)

The energies of the characteristic K-lines for the elements from scandium to zinc lie in the 4 - 10 keV region. The radiation detection is technically more simple in this energy region. Therefore, the radionuclide X-ray fluorescence analysis is more widely used for determination of the elements with atomic numbers /117 21 - 30. Not only the proportional counters, but also the scintillators and recently also the solid state detectors are used for the radiation detection.

Radiation of ^{55}Fe is advantageous for scandium, titanium and vanadium determination. If the sample matrix contains only light elements, an accuracy up to 0.01% can be achieved. The presence of a heavier element in the matrix causes a disturbing matrix absorption effect with respect to the excitation and fluorescence radiation; therefore, the analysis accuracy is then lower. Vanadium determination has reached 0.025% accuracy in the presence of iron [19]. Accuracies of 0.1 - 0.2% were achieved for chromium and manganese determination in steels, and for nickel and copper determination in copper alloys [19,20].

^{3}H/Zr was used as the excitation radiation source for copper, iron and nickel determination in ores [21, 22] and for iron determination in machine oils [23]. To isolate the Fe-K line from the scattered radiation is relatively simple; even a simple filter with an iron absorption edge is sufficient. In ores with an iron content of 0 - 50%, an accuracy of ± 0.4% was achieved after a one-minute measurement.

When ^{3}H/Zr is used as a radiation source for the iron, zinc or copper determinations in ores, it is necessary to eliminate the matrix absorption and enhancement effects [22]. Concentration of the neighbouring elements in ores changes strongly — as, for example, the iron concentration in zinc and copper ores. The two-channel nomogram calculation method can be used under laboratory conditions

for the measurement of the X-ray lines of zinc and iron or copper and iron. In the field, the analyser is replaced by a filter with absorption edge technique.

A remarkable accuracy was achieved in ore analysis with 1 - 5 minute measuring intervals [22]: ± 0.2 - 0.5% Fe in the 0 - 40% Fe content region for iron ores; ± 0.25% Zn and Fe in the 0 - 10% Zn and Fe content region in zinc ores; ± 0.1 - 0.4% Cu in copper ores with 0 - 15% Cu.

A bremsstrahlung source (^{3}H/Zr) was also utilized for nickel in the aluminum determination (Ni -K: 7.5 keV). Sensitivity was 1% Ni. The accuracy of a one-minute measurement in the 1 - 4% Ni range is 2% [23].

A flow analysis device was employed for the copper determination in copper ores [24]. Radionuclide ^{109}Cd was used; it excited, however, the iron lines together with the copper lines. Iron is often present as an ore impurity. A pair of balanced filters Fe -Ni, which select the energy region 7.11 - 8.33 keV (Cu -Kα: 8.05 keV), was utilized together with a proportional counter for the radiation detection. The absorption matrix effect, caused particularly by the iron impurities (up to 6%) disturbs the copper determination in copper ores. The intensity of the ^{109}Cd radiation source after transmission through the sample (I_t) was measured simultaneously with the copper X-ray fluorescence radiation (I_{Cu}). The ratio I_{Cu}/I_t is, theoretically, almost independent of the interfering element concentration. The following considerations were used for the derivation of the transmission correction: the Cu-K line intensity increases with increasing copper content in ore, but it decreases with a decreasing iron content. The intensity of transmitted radiation decreases with increasing content of copper and iron. When the sample thickness is chosen properly, the ratio I_{Cu}/I_t is independent of the iron concentration and sensitive to the copper content.

Powdered samples were used for the copper determination in ores. Absorption of the ^{109}Cd radiation in analysed samples was measured simultaneously to decrease the matrix absorption effect. A portable, battery-operated fluorescence analyser [10] was utilized for the copper determination in ores by radionuclide ^{109}Cd radiation. The presence of iron or cobalt disturbs the measurement. It is impossible to distinguish their characteristic lines by a NaI (Tl) scintillator spectroscopically. Therefore, a pair of balanced filters Ni (7.7 mg/cm^{-2}) and Co (8.5 mg/cm^{-2}) was employed for the selection of the fluorescence line energy. The absorption edges
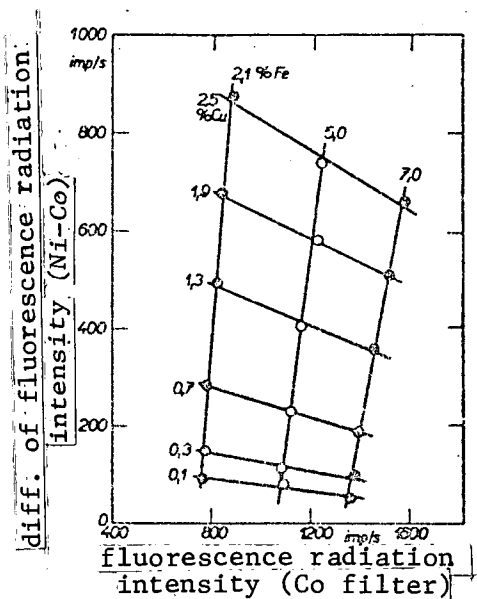
Figure 5. Nomographic determination of the copper content in ores and its dependence on iron content [10].

of the filters are: Co - 7.71 keV, Ni - 8.33 keV; the copper Kα line (8.04 keV) lies in this interval.

The matrix absorption effect, caused by the presence of iron, can be completely eliminated by the graphic solution with nomographs, shown in Figure 5. The difference in the impulse number for the filter pair Ni-Co is given on the ordinate axis. This quantity depends linearly on the content of both copper and iron. The pulse number after filtering with cobalt is on the abscissa axis. The statistical error, after 20 seconds measuring time, is 0.035% Cu and 0.05% Fe.

For cobalt and zinc excitations, the [109]Cd is advantageous; it produces by electron capture quantum radiation of 22 keV energy. Fluorescence radiation can be relatively easily discriminated from the scattered excitation radiation by a proportional counter [3].

The zinc content in zinc ores was determined by the radionuclide [109]Cd (0.5 m Ci) radiation and a proportional counter. A pair of balanced filters Cu -Ni <u>/119</u> was used to isolate zinc Kα-line [24].

A bremsstrahlung source [147]Pm/Al was utilized for the copper and nickel determination in water sludge [25] and for the cobalt determination in hydrocarbons [26]. The sensitivity of 10 ppm Co was ensured by the balanced filter pair Mn - Fe. The main hydrocarbon components are hydrogen and carbon, with traces of iron [27].

The proportional counter and one-channel amplitude analyser are used for analysis of Cu-Zn alloy by the ^{3}H/Zr bremsstrahlung excitation. The copper K-line (8.0 keV) is more excited than the tin L-line (3.4 keV). An accuracy of 0.33% was achieved in tin determination by a 100-second measurement in alloys with up to 50% Sn [27].

Analysis of the Cu-Zn alloys is somewhat difficult, because the elements form a pair of neighbours in the periodic system. The characteristic lines cannot be solved by the proportional counter and both elements are almost equally excited. A nickel filter (0.013 mm) absorbs the zinc K-line, and thus the copper content in the alloy can be measured. An accuracy of 0.9% copper was achieved by a 200-second measurements in alloys with 90% copper [27].

When elements of the IV period are determined, excitation caused by β-particles emitting radionuclides is sometimes used [28-33].

Determination of elements Ga-Ba.
(31<Z<57)

The most favourable conditions for the radionuclide fluorescence analysis are in the region of elements with medium values of the atomic number. The characteristic lines of the K-series in this region of elements Z:31-57 have energies of 9-33 keV. A large number of suitable radionuclides exists for the excitation of this energy; the radiation detection is not technically difficult. The sensitivity and accuracy of the element determination by methods of radionuclide X-ray fluorescence analysis are most favourable for the medium Z elements.

Scintillation detectors are mostly used for the detection of fluorescence radiation. However, examples of proportional counters or solid state detectors utilization can be found too.

^{109}Cd and ^{125}I are used for excitation of elements with atomic numbers 31-41. The latter is, however, disadvantageous for its relatively short half-life (60 days). The γ-radiation of ^{109}Cd can be employed for excitation of fluorescence radiation of molybdenum, technicium and ruthenium. However, their K-lines overlap with the scattered radiation during detection. Although an accuracy of 0.04% was achieved in molybdenum and niobium determination in steels and 0.03% in ores, this was possible only with the help of a pair of balanced difference filters [19].

Fast zirconium determination by radionuclide fluorescence analysis was utilized for different sand raw materials and zirconium concentrates [34]. The source of exciting radiation was ^{109}Cd. The sand raw materials, due to a relatively high iron and titanium content, have a high matrix effect. Matrix effects were eliminated /120

by nomographic interpolation of the zirconium fluorescence radiation and scattered excitation radiation. The radiation intensity was measured by a proportional detector and pulse counter. Concentrates were diluted by pure sand. To reduce the matrix effects, the ratio of intensities of the fluorescence radiation and scattered radiation was measured. With filters, an accuracy 1.5% of Zr was achieved in concentrates with 0.4 – 1.8% of Zr; in concentrates with <0.2% of Zr the accuracy achieved was 8%. The results were less favourable without filters. The relative error is 2.8% for 0.4 – 1.8% Zr; and for <0.2% of Zr the relative error is even 10%. All results refer to a one-minute measurement time.

Radionuclides [241]Am and [153]Gd are used for the excitation of elements heavier than ruthenium. Their γ-radiation, or occasionally, X-ray radiation from a suitable target, are utilized.

The tin content in solder (Sn–Pb) was determined by [241]Am γ-radiation; the tin K-line (25 keV) was measured. An accuracy of 8% was achieved during one-minute measurements [15] within the 1 – 5% tin range. Determination of the silver component in photographic emulsion AgBr by [241]Am is based on the intensity measurement of the silver K-line (22 keV) radiation. In one-minute measurements, 2% accuracy was obtained [27].

X-ray radiation, excited by γ-radiation, was employed for determination of small amounts of cadmium (0 – 0.3%) in zinc plates [35]. [153]Gd–Te was the source of X-ray radiation; intensity of the Cd Kα line was measured by a NaI(Tl) scintillation counter. A palladium filter 0.06 mm thick was used. The calibration curve is shown in Figure 6. Sensitivity of the analysis is 0.007% Cd.

Antimony in the 0 – 2% range was similarly determined in lead plates [35]. [153]Gd–Cs served as the X-ray radiation source, with cesium in the form of CsCl. The calibration curve is shown in Figure 7. A sensitivity 0.013% Sb was achieved.

The combination [153]Gd–Sb was utilized for silver determination, while [153]Gd–Te was used for cadmium determination in alloys. Tin in alloys was determined with an accuracy of 0.01%[19] by [241]Am–Cs[36] and [241]Am–Ba. A bremsstrahlung source [147]Pm/Al was also utilized for tin determination; accuracy of 0.1 – 0.03% [19, 37, 20] was achieved. Suitable combinations of γ radionuclide and the target were used
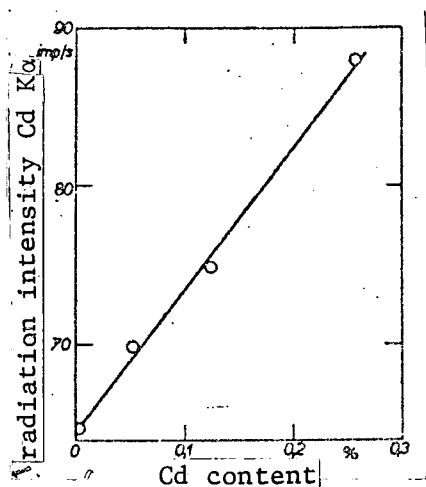
Figure 6. Calibration curve for cadmium in zinc determination [35].

Figure 7. Calibration curve for antimony in lead determination [35].

for excitation of elements between radium and barium. The combinations were chosen in such a way that the optimum excitation of the determined element [19, 38] was achieved.

Barium in geological samples was determined by the γ radiation (88 keV) of $^{127}Te^{39}$ radionuclide.

The $BaSO_4$ centent in different mixtures with qualitatively equivalent composition [40] was determined by the fluorescence method. γ radiation of radionuclides ^{170}Tm and ^{75}Se (0.4Ci) was used for the excitation. Barium fluorescence radiation was detected by the NaI (Tl) scintillation counter using a calibration curve [1, 40]. The change in the quantitative chemical matrix composition caused measurement errors of 1 - 2%.

Ingenious methods employ bremsstrahlung sources, where the β radionuclide and target element form a common molecule: ^{35}S/Ba in $BaSO_4$ form, and ^{14}C/Ba in $BaCO_3$ form. Antimony, tin and molybdenum in rocks were determined by these radiation sources in combination with a pair of balanced filters [41 - 44].

Lanthanide determination
(58<Z<71)

Radionuclide X-ray fluorescence analysis did not find a wider application for lathanide determination. The closeness of the lathanide characteristic energy lines, on the one hand, and an insufficient resolving power of the detectors, on the other hand, are the most decisive reasons for that. $^{170}Tm^{45}$ was used for the
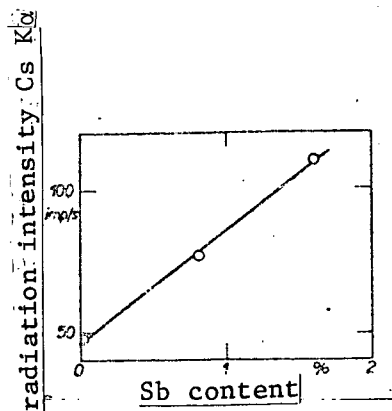
lathanide excitation. ^{241}Am is also suitable, both directly as a γ radiation source or, in combination with a suitable target, as a X-ray radiation source.

Determination of heavy elements
(Z>72)

Heavy elements can be determined in X-ray fluorescence not only by their K lines, but also by their L lines.

The characteristic K-series energy is in the 55 - 99 keV interval for the heavy elements (72<Z<92). γ radionuclides ^{57}Co, ^{153}Gd, ^{75}Se, ^{170}Tm [19, 41, 39, 46] could be used for the excitation. Scintillation and solid-state counters [3, 47, 48] are suitable for fluorescence radiation detection.

When exciting the fluorescence K-lines of heavy elements, it is difficult
to shield radiation with an energy of about 100 keV. Geometry with nonparallel axes is more suitable than co-axial geometry in such cases. The experimental arrangement with nonparallel axes, particularly with collimated radiation, allows a better elimination of the disturbing scattered radiation. The portion of scattered radiation is, especially in the matrix containing light elements, rather large at the energy of characteristic X-ray radiation of heavy elements. The geometry with nonparallel axes has, however, a disadvantageously lower geometrical excitation efficiency. Therefore, the radiation source must have greater activity.

The relative error of the tungsten determination in steels (^{170}Tm and ^{75}Se) is about 1% [40] for 2 - 20% of W content. Tungsten in steels was also determined by the ^{192}Ir excitation and K-line intensity measurement; the accuracy was ± 0.1% [49].

^{153}Gd [19] was used for lead determination in steels with an accuracy of 0.2%; lead and mercury in geological samples were determined by ^{75}Se and ^{170}Tm [50, 39, 46]. The accuracy of 0.1% [49] was achieved in lead determination in ore sludges and tungsten, lead and mercury determination in solutions; ^{192}Ir (E_γ-308keV) was used.

γ radiation of radionuclide ^{192}Ir was employed for lead determination in powder mixture PbS -SiO$_2$ -FeS$_2$-ZnS [49]. A PbS content below 2% can be determined with a relative accuracy of 5%.
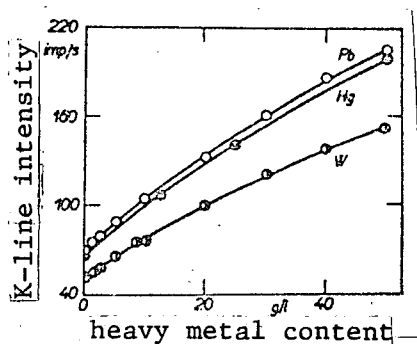
STOP HERE   STOP HERE   11

Figure 8. Curves showing the dependence of Pb,Hg,W K-line intensity on the concentration of their aqueous solutions [49].

Figure 8 shows the dependence of the K-line intensity of lead, mercury, and tungsten in water solutions on their concentration [49]. ^{192}Ir γ radiation was utilized for the excitation; an accuracy of 0.1% was achieved. It is assumed that a similar accuracy can be achieved for uranium and plutonium determination in water solutions.

Uranium in water solutions was determined by ^{57}Co radiation excitation in a geometrical arrangement with static and flowing samples [51]. ^{57}Co with a radiation energy of 122 keV is suitable for the uranium K-line excitation (97 keV). An accuracy of 1% was reached in solution with 0.02 - 1.0 gmol/l concentration. ^{57}Co radiation would be suitable for plutonium K-line excitation also; its absorption edge is 121.7 keV [51]. The solid-state detectors are effective for analysis of uranium solutions [52]. A large number of radionuclides — ^{75}Se, ^{141}Ce, ^{144}Ce-^{144}Pr, ^{154}Eu [40] — with suitable γ radiation energy for uranium K-line excitation was suggested for application in fluorescence analysis.

Bremsstrahlung radiation sources are sometimes used for X-ray fluorescence   /125 analysis of heavy elements. According to this, tungsten in tool steels was determined by ^{90}Sr -^{90}Y/Pb [40, 53, 54, 55]. An accuracy of 1.3% was achieved in a concentration range up to 20% of W.

A scintillation detector and single channel pulse analyser were used. Excitation by ^{147}Pm/Al bremsstrahlung was utilized for the tungsten determination in highly alloyed steels with Fe,Co, and Cr present. With 5 - 20% W, an accuracy of 2% was achieved in 20-second measurements.

X-ray radiation sources of γ radionuclide-target were used only rarely in heavy element analysis. It is difficult to find a suitable target material. For example, tungsten in solutions was determined by the ^{153}Gd/Pb [36] radiation source.

12

TABLE II.   REVIEW OF X-RAY RADIOFLUORESCENCE ANALYSES

Group of elements	Atomic no.	Element	Analysed sample	Reference
$T < 20$	12	Mg	cement	5, 6, 7
	13	Al	cement	5, 6, 7, 14, 15, 16, 17, 18
	14	Si	cement	5, 6, 7, 14, 15, 16, 17, 18
			coal	
	16	S	coal	10
	20	Ca	cement	10, 5, 6, 7, 8, 9, 14, 15, 16, 17, 18, 57
			mixtures	
			rocks	
			ore	
$21 < Z < 30$	21	Sc		19
	22	Ti	steel	19, 53, 58
			mixtures	
	23	V	steel	19, 58
			mixtures	
	24	Cr	steel	5, 19, 20, 53, 58
			mixtures	
	25	Mn	steel	19, 20, 53, 58
			mixtures	
	26	Fe	cement	10, 5, 6, 7, 8, 21, 22, 23, 59, 60
			ore	
			mixtures	
			rocks	
			oil	
	27	Co	mixtures	3, 26, 24
			hydrocarbons	
	28	Ni	aluminum	19, 20, 21, 22, 25, 39, 23, 58, 61
			ore	
			alloys	
			sludges	
	29	Cu	ore	27, 3, 22, 25, 24, 62, 63, 64
			alloys	
			concentrates	
	30	Zn	ore	27, 3, 22, 25, 24, 62, 63, 64
			alloys	
			concentrates	
			sludges	
			solutions	
$31 < Z < 57$	39	Y	mixtures	65
	40	Zr	sands	66, 34, 67
			concentrates	
			solutions	

TABLE II.   REVIEW OF X-RAY RADIOFLUORESCENCE ANALYSES
(Continuation)

Group of elements	Atomic number	Element	Analysed sample	Reference
$31 < Z < 57$	41	Nb	steel ore sludges mixtures	19, 53, 64
$31 < Z < 57$	42	Mo	steel ore mixtures solutions	19, 41, 42, 43, 44, 53, 64
	47	Ag	photomaterial	27, 36, 68
	48	Cd	zinc alloys	69, 36, 35, 70
	50	Sn	bronze barrel steel sludges, mixtures solutions	27, 19, 20, 36, 37, 41, 42, 43, 44, 62, 64, 68
	51	St	lead rocks	41, 42, 43, 44, 35
	56	Ba	mixtures rocks sludges solutions	39, 40, 64
$58 < Z < 71$	58 71	lanthanides	mixtures minerals	45, 61
$Z > 72$	72	Hf	solutions	66
	73	Ta	mixtures	47, 48
	74	W	steel mixtures solutions	47, 48, 36, 49, 40, 53, 54, 55, 68
	78	Pt	mixtures	47, 48
	79	Au	mixtures	47, 48
	80	Hg	rocks solutions	50, 39, 41, 46, 49
	82	Pb	brass steel rocks sludges solutions mixtures	50, 19, 47, 48, 39, 47, 46, 49, 53
	90	Th	mixtures	47, 48
	92	U	solutions	47, 48, 51, 40, 56, 52
	94	Pu		51

STOP HERE   STOP HERE

14

Miligram amounts of tantalum, platinum, gold, lead, tungsten, thorium and uranium were determined in model samples by ^{57}Co γ radiation and solid-state germanium detectors [47, 48].

X-ray fluorescence determination of heavy elements by their K-series lines is more advantageous than the utilization of the L-series lines. The former is almost uninfluenced by the inhomogeneity and grain size of the analysed samples [3]. On the other hand, a determination of heavy elements from their L-series lines is more accurate. The energy region of L-series lines is 7 - 14 keV; therefore, different radiation sources are used for L-series lines and K-series line excitations. For example, the radionuclide ^{241}Am with a cadmium target [56] was used for uranium determination in solutions using L-lines.

Review of radionuclide fluorescence analyses

X-ray fluorescence analytic methods with radionuclide fluorescence radiation excitation sources were used in a large number of analyses. The decisive factors for accuracy and sensitivity of the analysis are:

— atomic number of the determined element
— chemical composition of the analysed sample matrix
— geometrical arrangement of the radiation source, sample, and radiation detector
— type of radiation detector employed

Review of the elements (together with the sample type), determined by the radionuclide fluorescence analysis, is given in Table II.

Conclusion

This work is a continuation of the two preceding parts in the series on radio-nuclide X-ray fluorescence analysis. The first part described the principles of this analytic method and most commonly used radionuclide sources of excitation radiation. The second part described the detectors of the X-ray fluorescence radiation and the measuring technique.

STOP HERE   STOP HERE

The goal of this third and last part is to show, on a number of examples, the applicability of the method, and to document the importance of radionuclide X-ray fluorescence analysis as an instrumental analytic method.

REFERENCES

1. Varga Š. Chem. listy, Vol. 64, 1970, p. 1253.

2. Varga Š. Chem. listy, Vol. 65, 1971, p. 28.

3. Schiller P., J. Švitel, E. Havránek and E. Dejmková. Possibilities of X-ray fluorescence analysis in the CSSR. Komensky University, Bratislava 1968.

4. Tanemura, T. Jap. J. Appl. Phys., Vol. 3, 1964, p. 208.

5. LeTraon, J.Y. and G. Seibel. Int. J. Appl. Rad. Isotop., Vol. 14, 1963, p. 365.

6. Seibel, G. and J.Y. LeTraon. Int. J. Appl. Rad. Isotopes, Vol. 14, 1963, p. 259.

7. Kühn, W. Kerntechnik, Vol. 6, 1964, p. 239.

8. Lubecki, A. and M. Wasilewska. J. Radioanal. Chem., Vol. 1, 1968, p. 25.

9. Starnes, P.E. and J.W.C. Clark. Symp. Radioisotop. Instr. in Industry and Geophys., Warsaw 1965.

10. Rhodes, J.R. Proc. 2. Symp. Low Energy X- and Gamma Sources and Appl., Austin, 1967.

11. Rhodes, J.R. Analyst, Vol. 91, 1966, p. 683.

12. Robert, A. Rapport CEA-R 2539, Saclay, 1964.

13. Robert, A. and P. Martinelli. Proc. Symp. Radiochem. Methods of Analysis, IAEA Salzburg, 1964.

14. Imamura, H., K. Uchida and H. Tominaga. Radio — Isotopes, Vol. 14, 1965, p. 286.

15. Uchida K. Radioisot. Inst. Ind. Geophys., Vol. 1, 1966, p. 113.

16. Tominaga, H. and K. Uchida. Proc. 6th Jap. Conf. Radioisot.,1964, p. 167

17. Imamura H., K. Uchida and H. Tominaga. Proc. 6th Jap. Conf. Radioisot., 1964, p. 490.

18. Imamura, H., K. Uchida and H. Tominaga. Radioisotopes, Vol. 13, 1964, p. 355.

19. Rhodes, J.R., T.W. Packer and I.S. Boyce. Symp. on Radioisotope Instruments in Industry and Geophysics, IAEA, Warsaw 1965.

20. Darnley, A.G. and C.C. Leamy. Symp. Radioisot. Instr. in Industry and Geophys. Warsaw, 1955.

21. Niewodniczanski, J. Symp. Radioisot. Inst. in Industry and Geophys., Warsaw, 1965.

22. Florkowski, T. Symp. Radiochem. Meth. Analysis, Salzburg, 1964.

23. Florkowski, T. and J. Gilewicz. Nukleonika, Vol. 7, 1962, p. 793.

24. Rhodes, J.R., T.G. Ahier and D.O. Poole. AERE — R 4474, 1964.

25. Rhodes, J.R., I.G. Ahier and D.O. Poole. Symp. Anal. Instr. Windscale, 1963.

26. Rhodes, J.R., T. Florkowski and J.F. Cameron. AERE — R 3925, 1962.

27. Cameron, J.F. and J.R. Rhodes. Nucleonics, Vol. 19, 1961, p. 53.

28. Reiffel L. Nucleonics, Vol. 13, 1955, p. 22.

29. Cook G.B., C.E. Mellish and J.A. Payne. Int. Conf. Peaceful Uses Atom. Energy, Geneva, Vol. 19, 1958, p. 127.

30. Enomoto, S. and C. Mori. Jap. J. Appl. Phys., Vol. 2, 1963, p. 274.

31. Leontiadis, L. Construction of a Beta X — fluorescence Gauge for Chemical Analysis, CEA-R 2970, 1966.

32. Tanemura, T. Jap. J. Appl. Phys., Vol. 5, 1966, p. 51.

33. Enomoto, S. and T. Tanemura. Symp. Radioisot. Instr. in Industry and Geophysics, Warsaw, 1965.

34. Holyńska, B. and L. Lenger. Anal. Chim. Acta, Vol. 40, 1968, p. 115.

35. Hope, J.A. and J.S. Watt. Rept. AAEC/TM, 1964, p. 260.

36. Watt J.S. Int. J. Appl. Rad. Isotop., Vol. 18, 1967, p. 383.

37. Bowie, S.H.V., A.G. Darnley and J.R. Rhodes. Trans. Inst. Mining Metall., Vol. 74, 1964-1965, p. 361.

38. Carr-Brion, K.G. and J.R. Rhodes. Instr. Pract., 1965, 1007.

39. Mejer, V.A. and N.S. Machabcev. Voprosy rudnoy geofiziki, Vol. 6, 1965, p. 34.

40. Górski, L. Kernenergie, Vol. 6, 1963, p. 710.

41. Mejer, V.A. Voprosy rudnoy geofiziki, Vol. 6, 1965, p. 68.

STOP HERE   STOP HERE

42.   Očkur A.P.   Voprosy rudnoy geofiziki, Vol. 6, 1965, p. 43.

43.   Očkur A.P., E.P. Leman and G.A. Pšeničnyj.   Voprosy rudnoy geofiziki, Vol. 6, 1965, p. 17.

44.   Očkur A.P., E.P. and G.F. Kommissarževskaja.   Voprosy rudnoy geofiziki, Vol. 6, 1965, p. 87.

45.   Jakubovič, A.J. and V.J. Zalesskij.   Zavodskaya lab., Vol. 27, 1961, p. 713.

46.   Bolšakov, A.Ju., A.P. Očkur and V.N. Orlov.   Voprosy rudnoy geofiziki, Vol. 6, 1965, p. 80.

47.   Bowman, H.R.   Science, Vol. 151, 1966, p. 562.

48.   Hyde, E.K., H.R. Bowman and D.H. Sisson.   Analytical Capabilities of a Semiconductor X-ray Emission Spectrometer UCRL-16 845, 1966.

49.   Martinelli, P. and P. Blanquet.   Symp. Radiochem. Meth. Anal. IAEA, Salzburg, 1964.

50.   Tanemura, T.   Jap. J. Appl. Phys., Vol. 2, 1963, p. 347.

51.   Forberg, S. and A.R. de Ruvo.   Symp. Radiochem. Meth. Anal. IAEA, Salzburg, 1964.

52.   Beach Glos, M.   Nucleonics, Vol. 22, 1964, p. 50.

53.   Górski, L. and A. Lubecki.   Symp. Radiochem. Meth. Anal. IAEA, Salzburg, 1964.

54.   Górski, L.   Second Crackow Symposium on Radio Isotopes in Technology, Spala, 1963, p. 33.

55.   Górski, L.   loc. cit, 1963, p. 34.

56.   McKay, K.J.H.   J. Inorg. Nucl. Chem., Vol. 19, 1961, p. 171.

57.   Martinelli, P.   Bull. inf. Sci. Techn. CEA, No. 92, 1965.

58.   Karttunen, J.O.   Anal. Chem., Vol. 36, 1964, p. 1277.

59.   Wagner, A., P. Eck and J. Hilger.   Vol. 10, 1967, p. 70.

60.   Emmerich, R., J. Gilewicz and B. Holyńska.   Zavodskaya lab., Vol. 32, 1966, p. 159.

61.   Karttunen, J.O. and D.J. Henderson.   Anal. Chem., Vol. 37, 1965, p. 307.

62.   Rhodes, J.R.   Symposium on Radio-chemical Methods of Analysis, IAEA, Salzburg, 1964.

63.   Dziunikowski, B.   Nukleonika, Vol. 9, 1964, p. 829.

STOP HERE   STOP HERE

64. Carr-Brion, K.G. Inst. Min. Metall., Vol. 76, 1967, p. C 94.

65. Klecka, J.F. Anal. for Y width a semiconductor X-ray emmssion Spectrograph and an I^{125} source UCRL-17144, 1966.

66. Seibel, G. Int. J. Appl. Rad. Isotopes, Vol. 15, 1964, p. 25.

67. Holyňska, B. and L. Langer. Proc. of XIV. Colloquium Spectroscopicum internationale, Debrecen, 1967.

68. Rhodes, J.R. AERE — R 4457, 1963.

69. Radiochemical Manual, 2. vyd. Radiochem. Centre, Amsterdam 1966.

70. Hope, J.A. J.S. Watt. Int. J. Appl. Rad. Isotopes, Vol. 16, 1965, p. 9.

71. Mellish, C.E. and J.A. Payne. Konf. Kodaň, 1960 Ref. RICC/21.